Temperature dependence of absorption edge in p-type porous silicon

Article *in* Physics of Low-Dimensional Structures · January 1998

CITATIONS
0

READS
7

2 authors, including:

Alpan Bek
Middle East Technical University
66 PUBLICATIONS **939** CITATIONS

SEE PROFILE

Temperature Dependence of Absorption Edge in p-Type Porous Silicon

A.Bek and A.Aydinli

Physics Department, Bilkent University, Ankara, 06533, Turkey

The observed blue shift of both the PL and the absorption edge in porous silicon is generally understood within the framework of quantum confinement of carriers in small crystallites where reduction of the density of states in the vicinity of c-Si band edge as well as increased oscillator strength, lead to higher direct radiation rates. Temperature dependence of transitions in semiconductors may provide additional information to clarify the nature of the recombination mechanism in porous silicon. In this work, we have studied the temperature dependence of the absorption edge of free standing porous films in the photon range of 3.1–1.35 eV and in the temperature range of 8.5–300 K. We find a smoothly varying spectral dependence of transmission on photon energy without any sharp features down to 8.5 K. The absorption edge for all samples studied show a gradual blue shift with decreasing temperature. Comparison with c-Si shows that red luminescing porous Si preserves the indirect nature of the c-Si band gap.

1. Introduction

The occurrence of strong visible photoluminescence (PL) in porous silicon is now well established [1]. Many tools have been used in an attempt to clarify the origins of this strong PL. While the detailed understanding of the recombination process is still lacking, spectral measurements of the absorption behavior of porous silicon showing clear evidence of blue shift of the absorption edge as a function of porosity is generally accepted to be due to quantum confinement, the consequences of which are reduced electronic density of states and increased oscillator strength. Aided by the breakdown of the k selection rules, quantum confinement can lead to enhanced direct transition rates as well as a blue shift in the absorption edge of porous Si. Absorption experiments in microporous Si have already shown [2] an exponential increase in absorption coefficient with temperature not expected of indirect semiconductors.

This behavior has been attributed to the effects of quantum confinement coupled with size distribution of the crystallites. Further insight into the behavior of absorption may be gained through studying its temperature dependence.

2. Experimental

Free standing microporous layers have been prepared from p-type boron doped (001) Si with a resistivity of 1–10 Ωcm. Aluminum was evaporated and annealed as a back contact prior to anodization. A polyethylene cell was used to hold the ethanoic hydrofluoric solution with Pt plate acting as the cathode. Several mixing ratios of HF and ethanol were used. Since as the HF concentration decreases porosity increases rapidly it was only possible to obtain free standing films for (HF:ETH) ratios of (1:1) through (4:1). Typical etch current density was 45 mA/cm^2 except in the case of 1:1 solutions where the etch current density was 15 mA/cm^2. Typical etch times were 60 min. in order to obtain thick sample of the order of 100 microns or more. Only for 1:1 samples, the etch times were increased to 3 hours due to low etch current density. Sample thickness ranged from 100 to 160 microns. Porosity of samples ranged from 60 to 75 % and was measured using gravimetric method. After the etching, samples were detached from the substrate by an electropolishing step. Samples were then rinsed in ethanol and dried with dry nitrogen. Attention was paid to take the measurements immediately after preparation and were finished usually within a few hours. Fourier Transform Infrared Spectroscopy, PL and Raman spectroscopy were used in addition to optical absorption measurements with a

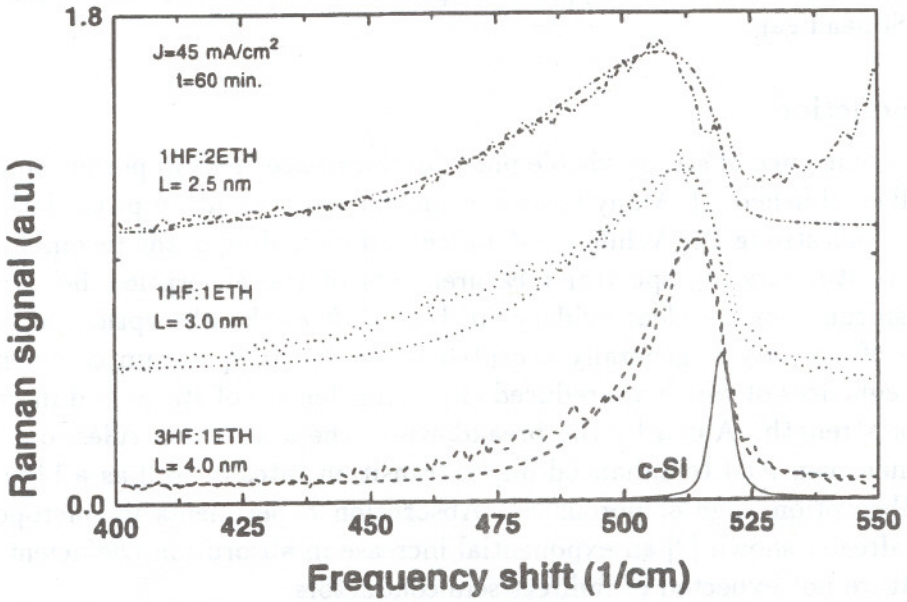

Figure 1. Raman scattering from porous Si prepared with different HF concentrations and lineshape analysis with different crystallite sizes using Eq.1.

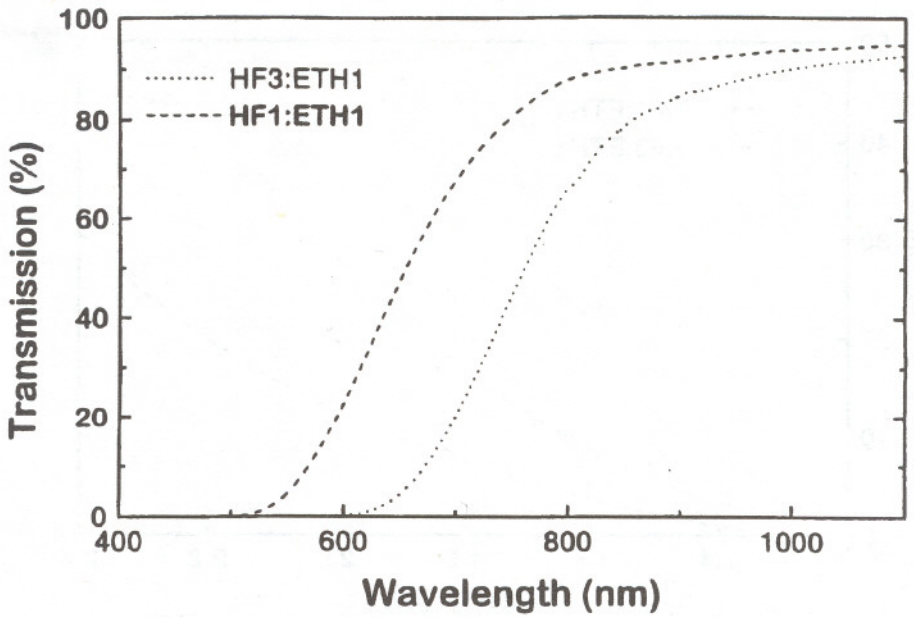

Figure 2. Optical transmission curves of porous Si prepared with different HF concentrations at room temperature.

UV-Visible Varian Cary5 spectrophotometer to characterize the samples. Reflection measurements in the visible on limited samples were done using a fiber based reflectometer. For low temperature measurements, samples were mounted on a copper disk with a pinhole and placed in a closed cycle refrigerator capable of reaching 8.5 ± 0.5 K.

3. Results

Free standing films of porous Si was first evaluated by FTIR spectroscopy in the range of 400–4000 cm^{-1}. We find that spectra are dominated by Si-H bands with small amounts of oxygen contamination in some of the samples. This is most likely due to exposure of the sample to atmosphere prior to the measurements. Photoluminescence was excited using an Ar^+ laser. Typically samples prepared with HF:ETH ratios of 1:1 or larger give a broad spectra in the near infrared approximately centered at 750 nm. Samples prepared with lower concentrations of HF (1:3) show narrower PL bands centered near 550 nm. However, the large porosities of these samples do not allow obtaining free standing films and were not used in this work.

Porous Si films were also studied by Raman spectroscopy to determine the particle sizes. It is well known that it is possible to deduce an average particle

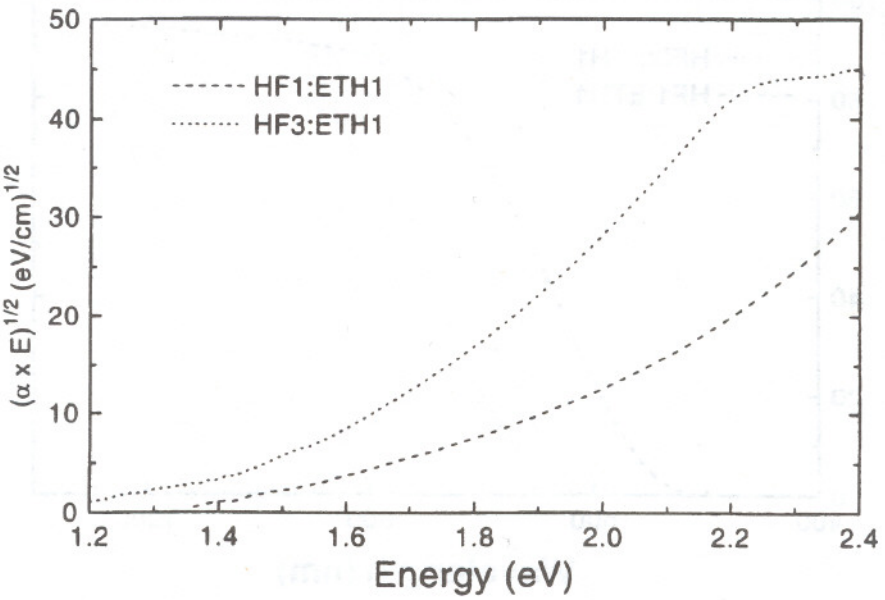

Figure 3. $(\alpha E)^{1/2}$ vs. E curves for porous Si prepared at two different HF concentrations.

size from the one-phonon Raman spectrum of porous Si. Such line shape analysis may yield not only an average particle size but may also allow to distinguish the shape of the particles involved in the scattering process, whether spherical or cylindrical. Typical spectra for porous Si samples prepared with different HF:ETH concentrations are given in Fig.1. We find the broadening of the first order Raman peak as the HF concentration decreases. The peak positions shift towards lower frequencies as well. We fit the lineshape to [3]:

$$I(\omega) \simeq \int \frac{d^3q|C(0,q)|^2}{(\omega - \omega(q))^2 + (\Gamma_0/2)^2}.$$

Here, $|C(0,q)|^2 \simeq \exp(-q^2L^2/4)$, q is expressed in units of $2\pi/a$ and L in units of a which is the lattice constant of Si. Γ is the natural linewidth (~ 3.5 cm^{-1}) and $\omega(q)$ is the dispersion relation for optical phonon in c-Si. Since the expected peak shifts as a function of peak widths saturate much faster for cylindrical particles, we find from a plot of peak shift vs peak widths that our samples are composed of spherical crystallites. For the etching conditions used in this study average diameters vary from 2.5 nm to 0.5 nm and decrease with decreasing HF concentration. We see that the lineshape fit is much better for the smallest average crystallite size while in the case of larger crystallite sizes the fit becomes not so good indicating larger size distributions in these cases.

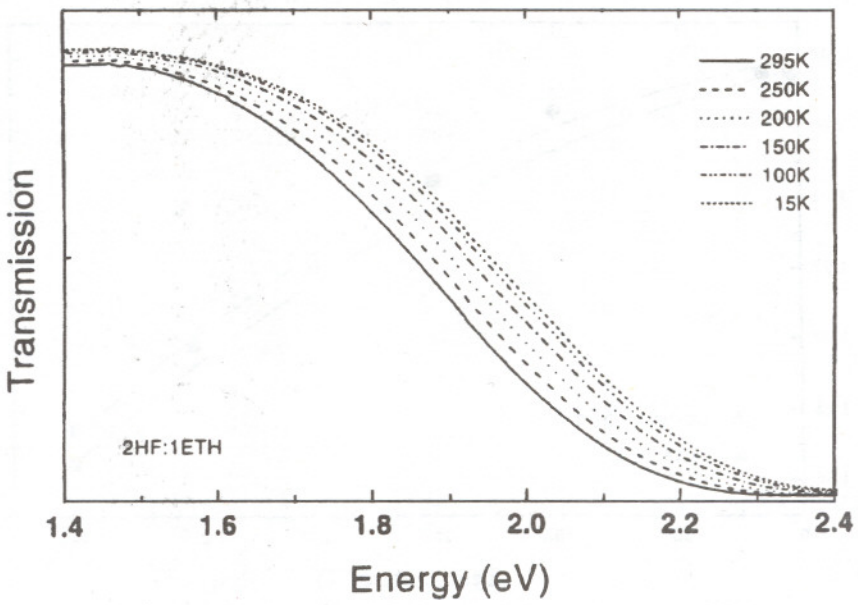

Figure 4. Temperature dependence of transmission in porous Si prepared in 2HF:1ETH solution.

Porosities of the samples prepared with HF:ETH concentrations (1:1) through (1:4) range from 73 to 60 %. Reflection measurements were done on selected samples using a fiber based reflectometer in the range of 600–1100 nm. A silver mirror was used as a reference. The observed specular reflection (< 4 %) is small with even weaker reflection in the region of strong absorption. However, this reflection does not include scattering effects which may be essential. From the magnitude of transmitted light, we estimate that the combination of reflection and scattering can be neglected for the purposes of this work.

Transmission data at room temperature taken from the samples prepared with different HF concentrations is shown in Fig.2. We observe the onset of strong absorption (transmission below 1 %) between 600–650 nm. We note that transmission increases smoothly with the wavelength and tends to saturate beyond 800 nm. We also note that the samples prepared with lower concentrations of HF has higher absorption at the same energies than those prepared with higher concentrations of HF. This behavior scales with crystallite sizes as shown in the Raman analysis above.

One can extract the absorption coefficient from above data using the relationship between transmission, absorption and the thickness of the material and porosity [4]. The spectral dependence of the absorption of porous Si is different from c-Si. Between 1.5 to 2.4 eV the absorption coefficient depends

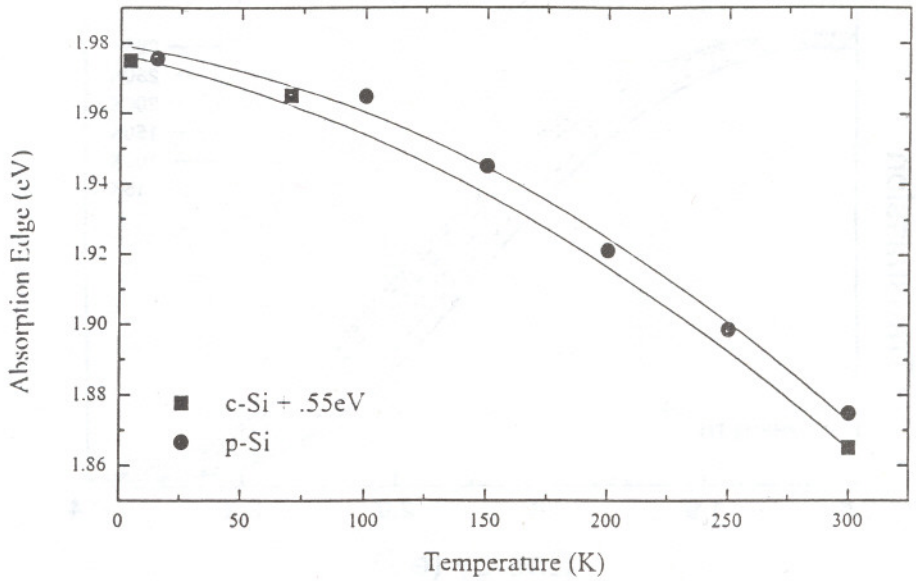

Figure 5. Absorption edge of porous Si prepared in 2HF:1ETH solution compared with c-Si.

exponentially on the energy. This is in agreement with previous results. Below 1.5 eV absorption coefficient becomes much more linear indicating the presence of larger crystallites which behave as an indirect semiconductor. To make this point clear we plot the $\sqrt{\alpha\hbar\omega}$ as a function of $\hbar\omega$ in Fig.3. The nonlinear behavior not expected of an indirect semiconductor becomes clear especially at high energies.

An example of temperature dependence of transmission in porous Si is given in Fig.4. Note that a smooth variation of the transmission is preserved as the sample is cooled down to 10 K. We have cooled samples down to 8.5 K without observing any sharp features in the transmission spectra. Note that as the sample cools the absorption edge shifts towards the blue as expected in c-Si. We analyzed several samples prepared with different etching solutions. Defining absorption edge at 50 % of the transmitted intensity, we plot the temperature dependence of absorption edge of porous Si and similarly defined absorption edge of c-Si, in Fig.5. The curve for c-Si was shifted by a constant amount to match the value observed for porous Si at low temperatures. In spite of a small vertical downward shift of the c-Si curve, assumed to be within experimental error, the general temperature dependence of the absorption edge of c-Si mimics that of porous Si except for the offset in energy by 0.55 eV suggesting that porous Si luminescing in the deep red-near IR portion of the electromagnetic spectrum

preserves the indirect nature of c-Si. We suggest further that the energy by which the c-Si absorption edge is to be blue shifted (0.55 eV in this case) can be understood within the quantum confinement model. We note that this energy scales inversely with particle sizes which further confirms the role of quantum confinement in absorption mechanism of porous Si.

4. Conclusions

Measurement of the temperature dependence of the absorption edge provides an important tool to understand the nature of the absorption process in porous silicon. The indirect nature of absorption in porous silicon is confirmed in this study while the spectral and temporal dependence of absorption is complicated by the size distribution of the crystallites in the films.

Acknowledgements

The authors would like to acknowledge the support of TUBITAK under Grant No. TBAG–1244.

References

[1] See for example; *Porous Silicon Science and Technology*, Eds: J.C.Vial, J.Derrien (1995), Springer Verlag; D.Lockwood, Solid State Commun., 98 (1995) 879.

[2] I.Sagnes et.al, Appl. Phys. Lett., 62 (1993) 1155.

[3] I.H.Campell and P.M.Fauchet, Solid State Commun., 58 (1986) 739.

[4] D.Kovalev et.al. J. Appl. Phys., 80 (1996) 5978.